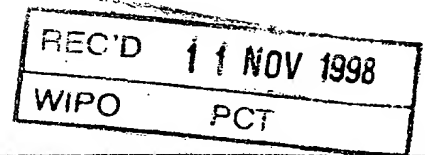




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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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International Application No. **PCT/IL 97 / 00391**International Filing Date **27 NOVEMBER 1997**
(27.11.97)ISRAEL PATENT OFFICE
PCT International Application
Name of receiving Office and "PCT International Application"Applicant's or agent's file reference
(if desired) (12 characters maximum) PDNBox No. I TITLE OF INVENTION
COATING SYSTEM FOR SUBSTRATES

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

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NETHERLANDSState (i.e. country) of residence:
NETHERLANDSThis person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

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☐ applicant only☒ applicant and inventor☐ inventor only (If this check-box is marked, do not fill in below.)State (i.e. country) of nationality:
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The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

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The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM		Further priority claims are indicated in the Supplemental Box <input type="checkbox"/>	
The priority of the following earlier application(s) is hereby claimed:			
Country (in which, or for which, the application was filed)	Filing Date (day/month/year)	Application No.	Office of filing (only for regional or international application)
item (1) ISRAEL	12 October 1997 (12-10-97)	121951	
item (2)	()		
item (3)	()		
Mark the following check-box if the certified copy of the earlier application is to be issued by the Office which for the purposes of the present international application is the receiving Office (a fee may be required):			
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Box No. VIII CHECK LIST			
This international application contains the following number of sheets: 1. request : 4 sheets 2. description : 8 sheets 3. claims : 5 sheets 4. abstract : 1 sheets 5. drawings : 0 sheets Total : 18 sheets		This international application is accompanied by the item(s) marked below: 1. <input type="checkbox"/> separate signed power of attorney 5. <input type="checkbox"/> fee calculation sheet 2. <input checked="" type="checkbox"/> copy of general power of attorney 6. <input type="checkbox"/> separate indications concerning deposited microorganisms 3. <input type="checkbox"/> statement explaining lack of signature 7. <input type="checkbox"/> nucleotide and/or amino acid sequence listing (diskette) 4. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 8. <input type="checkbox"/> other (specify): _____	
Figure No. _____ of the drawings (if any) should accompany the abstract when it is published.			
Box No. IX SIGNATURE OF APPLICANT OR AGENT			
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).			
 FENSTER, Paul AGENT			

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COATING SYSTEM FOR SUBSTRATES

FIELD OF THE INVENTION

The present invention is related to the field of printing and in particular to a method of coating substrates to improve adhesion of toner images thereto.

BACKGROUND OF THE INVENTION

Problems of transfer and adhesion of toner images and in particular of liquid toner images, to substrates, is well known. Transfer of images may be effected by electrostatic transfer of toner particles to the substrate, either from an imaging surface such as a photoreceptor or from an image transfer member. Alternatively, image transfer may be effected by heat and pressure, generally from an intermediate transfer member to which the image is first transferred from the imaging surface. Image transfer from an intermediate transfer member, on which the image is generally in a molten state, is often problematic. Usually, some treatment of the substrate surface is required in order to enable good transfer and fixing.

Transfer and adhesion of toner is improved by chemical compatibility of the toner and the substrate for example, chemical bonding by acid-base interaction or chemical similarity leading to mutual bonding.

A common solution to transfer and adhesion problems is the coating of a substrate with an adhesion enhancer, which has an affinity for both the toner material and the substrate. For example, the adhesion of the above mentioned toner types to PET and BOPP can be greatly enhanced by coating the substrates with a layer of Macromelt 6239 (Henkel) which is an amine terminated polyamide. This material adheres well to the substrate and has a high affinity for the toner particle polymer as well. However, it has been found that the shelf life of such coated substrates is limited and the quality of the transfer of toner from an intermediate transfer member to the substrate degrades with time. This aging process of the coating does not seem to effect the adhesion of images which are already transferred to the substrate.

However, as is well known in the art, such substrate processing does not always lead to satisfactory results, especially in digital electrostatic printing.

SUMMARY OF THE INVENTION

One aspect of the present invention is a novel approach to the improvement of transferability and/or adhesion of images to substrates, especially plastic substrates.

In a broad view of the invention, a double coating is employed, with an underlayer having a high affinity for the substrate and an overlayer having a high affinity for the toner material. The two layers have a high affinity for each other.

In an exemplary embodiment of this aspect of the invention, the underlayer is a layer
5 of an amine terminated polyamide such as Macromelt 6239 (Henkel) which was mentioned in the background of the invention. The upper layer is formed of material which has a high affinity for toner particles and which is also adheres well to the underlayer. As indicated above, an amine terminated polyamide has a high affinity for a wide range of materials so that this seldom is a problem. Furthermore, the above mentioned deterioration of the properties of
10 the amine terminated polyamide with time does not exist when it is coated with the overlayer.

Exemplary materials which are useful as overlayers include ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer. It is noted that these materials adhere rather poorly to untreated PET, BOPP, polycarbonate, polyethylene and vinyl. For some applications it is useful to reduce the degree of acidity of the ethylene acrylic
15 acid copolymer, preferably by Saponification to a level of preferably between 8 and 18% acrylic acid comonomer weight percent, more preferably between 10 and 16%. Unmodified material typically has a acrylic acid comonomer weight percent of 20%.

A second aspect of the invention relates to substrates which are coated with ethylene acrylic acid copolymer, polyvinyl pyridine or styrene butadiene copolymer, and especially to
20 substrates coated with ethylene acrylic acid copolymer with reduced acidity. Such coated substrates may, in some preferred embodiments of the invention, be plastic substrates such as PET or BOPP or, in other embodiments of the invention, may be paper.

A third aspect of the invention relates to the printing of images, preferably toner images and more preferably liquid toner images, on substrates of the invention or which are
25 produced in accordance with the invention. This printing is preferably by transfer of the toner images to the substrate from an intermediate transfer member, to which it was transferred from an imaging surface. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under
30 the trade name of Surlyn, by Dupont.

There is therefore provided in accordance with a preferred embodiment of the invention, a substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;
an underlayer coating, on the sheet of plastic, comprising a first polymer material;
an overlayer coating, on the underlayer, comprising a second polymer material and
having an outer surface to which a toner image can be fused and fixed.

5 Preferably, the sheet of plastic is PET. Alternatively, the sheet of plastic is BOPP.
Alternatively, the sheet of plastic is polyethylene. Alternatively, the sheet of plastic is vinyl.
Alternatively, the sheet of plastic is polycarbonate.

In a preferred embodiment of the invention, the overlayer comprises ethylene acrylic
acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid
10 comonomer percentage weight of less than 18%. Alternatively, the ethylene acrylic acid
copolymer has an acrylic acid comonomer percentage weight of less than 16%.

Alternatively or additionally, the ethylene acrylic acid copolymer has an acrylic acid
comonomer percentage weight of more than 8%. Alternatively, the ethylene acrylic acid
copolymer has an acrylic acid comonomer percentage weight of more than 12%.

15 In a preferred embodiment of the invention, the overlayer comprises polyvinyl
pyridine. Alternatively, the overlayer comprises styrene butadiene copolymer.

In a preferred embodiment of the invention, the underlayer comprises amine
terminated polyamide. Alternatively, the underlayer comprises a silane coupling agent.
Alternatively, the underlayer comprises amino propyl triethoxy silane.

20 In a preferred embodiment of the invention, the underlayer has a weight of between 0.1
and 1 grams per square meter. Alternatively or additionally, the underlayer has a weight of
between about 0.3 and 0.5 grams per square meter.

In a preferred embodiment of the invention, the overlayer has a weight of between 0.1
and 10 grams per square meter. Alternatively or additionally, the overlayer has a weight of
25 between 0.2 and 2 grams per square meter. Preferably, the overlayer has a weight of between
about 0.25 and about 0.35 grams per square meter.

There is also provided in accordance with a preferred embodiment of the invention, a
method of producing a coated substrate which a toner image can be adhered comprising:

30 coating a sheet of plastic with a first polymer material as an underlayer;
overcoating the underlayer with a second polymer material to form an overlayer
coating on the underlayer, the overlayer having an outer surface to which a toner image can be
adhered and fixed. Preferably, the coated substrate is a substrate as described above. There is

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also provided in accordance with a preferred embodiment of the invention, a substrate produced according to the above described method.

There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet chosen from the group consisting of PET, BOPP, polycarbonate, polyethylene and vinyl and an outer coating chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

Preferably, the sheet is a PET sheet. Alternatively, the sheet is a BOPP sheet. Alternatively, the sheet is a polycarbonate sheet. Alternatively, the sheet is a polyethylene sheet. Alternatively, the sheet is a vinyl sheet.

Preferably, the coating comprises polyvinyl pyridine. Alternatively, the coating comprises styrene butadiene copolymer. Alternatively, the coating comprises ethylene acrylic acid copolymer. Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

There is also provided in accordance with a preferred embodiment of the invention, a substrate comprising a sheet and a coating of ethylene acrylic acid copolymer having an acrylic acid comonomer percentage weight of less than 18%.

Preferably, an ethylene acrylic acid copolymer, as described above, has an acrylic acid comonomer percentage weight of less than 16%. Alternatively, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.

Preferably, the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 12%.

Preferably, the coating, as described above, has a weight of between 0.1 and 0.4 grams per square meter. Preferably, the coating has a weight of between about 0.25 and about 0.35 grams per square meter.

There is also provided in accordance with a preferred embodiment of the invention, a printing method comprising:

providing a substrate, as described above; and

printing a toner image on the substrate.

Preferably, the toner image is a liquid toner image. Alternatively or additionally, printing comprises transferring the toner image to the substrate using heat and pressure. Alternatively, printing comprises electrostatically transferring the toner image to the substrate.

In a preferred embodiment of the invention, the printing method comprises:

forming the image on an image forming surface;

transferring the image from the image forming surface to an intermediate transfer member; and

transferring the image from the intermediate transfer member to the substrate.

5

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A substrate according to a preferred embodiment of the present invention, on which a toner image is to be printed, comprises a plastic or other sheet coated with an underlayer having a high affinity for the substrate and an overlayer having a high affinity for the toner material. The two layers have a high affinity for each other.

10

One preferred, but non-limiting, method for producing such a substrate uses an underlayer of amine terminated polyamide and an overlayer of ethylene acrylic acid copolymer.

The underlayer

15 To 950 grams of 1-Propanal add 50 grams of Macromelt 6239 (Henkel), amine terminated polyamide, while stirring the mixture. Heat the material to between 40°C and 50°C until a homogeneous and clear 5% solids solution is obtained.

This material is applied to a substrate (for example an optionally corona treated BOPP substrate) by coating the substrate with the 5% solids solution and allowing the solution to dry, leaving a coating of preferably between about 0.1 and 0.3 grams of solid per square meter.

20

This coating should be uniform. The coating may be applied by any one of the available methods of coating and, for example, using a rotogravure coating system. Alternatively a flexographic printing system can be used to apply the coating with the settings of the printer controlling the thickness of the coating. However any other suitable coating process (double blade direct applicator, etc.) can be used. Other solution concentrations and other variations on

25

the above described method can also be used.

While thinner and thicker coatings could be used, thinner coatings are not always effective and thicker coatings are more difficult to apply and expensive.

After application of the solution the coating is dried, preferably by an integral heater in the coating apparatus.

The overlayer

To 465 gm of deionized water add 200 g of isopropyl alcohol. This reaction is exothermic. After the mixture cools, add it to 335 g of a dispersion of MP 4990 (32-35%) as supplied by Michelman.

5 The dispersion is coated onto the underlayer by any convenient coating process, as for the underlayer, to give a coating of between approximately 0.3 - 0.5 grams per square meter although thinner coatings can be used.. If a double coating apparatus is available, the overlayer may be applied immediately over a dried underlayer.

10 After application of the overlayer solution the coating is dried, preferably by using the dryer integral in the coater. Other drying methods can also be used.

While the above formulation of overlayer material is suitable for printing on web fed material, it will adhere to surfaces with which it comes into contact, while hot, after printings, as, for example, an exit roller. To reduce the hot adhesivity, the degree of acidity of the ethylene acrylic acid copolymer, is reduced, preferably by Saponification to a level of
15 preferably between 8 and 18% acrylic acid comonomer weight percent, more preferably between 10 and 16%. Unmodified material typically has a acrylic acid comonomer weight percent of 20%. This modified material can be used to directly coat paper and plastic substrates which do not require the adhesion promotion properties of the underlayer.

20 Other underlayer materials, for example, a silane coupling agent such as amino propyl triethoxy silane, may be used. The primary requirement for an underlayer is that it have high adhesion to the substrate and to the overlayer.

Other suitable overlayer materials include Polyvinyl pyridine (Molecular weight 40,000 to 200,000) (Scientific Polymer Products). Additionally Styronal PK 8717 (BASF) (styrene butadiene copolymer) can be used as the overlayer. These material are preferably
25 coated at a weight of approximately 0.5 grams per square meter.

Various bonding mechanisms can be utilized in various embodiments of the present invention. In the above example, the underlayer and overlayer are base and acid respectively. The toner described below is also acidic; however, the toner forms a strong chemical bond with the overlayer. Other materials, in accordance with preferred embodiment of the
30 invention, utilize other types of bonding.

In general, a coating thickness (after drying) of between 0.1 to 10 micrometers is preferred. More preferably, the thickness is between 0.2 to 2 microns.

The coated substrates of the present invention are useful with a wide range of toner material which do not transfer easily to and/or adhere well to PET and BOPP. Preferred toners are based on one or more of ethylene vinyl acetate (EVA) copolymers, copolymers of ethylene and α , β - ethyleneically unsaturated acid selected from the group consisting of acrylic and methacrylic acids and ionomers such as are produced under the trade name of Surlyn, by Dupont.

One preferred method of forming a toner is the following:

1) Solubilization

1400 grams of Nucrel 925 (ethylene copolymer by Dupont) and 1400 grams of Isopar L (Exxon) are thoroughly mixed in an oil heated Ross double planetary mixer at at least 24 RPM for 1.5 hours, with the oil temperature at 130°C. 1200 grams of preheated Isopar L is added and mixing is continued for an additional hour. The mixture is cooled to 45°C, while stirring is continued, over a period of several hours, to form a viscous material.

2) Milling and Grinding

762 grams of the result of the solubilizing step are ground in a 1S attritor (Union Process Inc. Acron, Ohio), charged with 3/16" carbon steel balls, at 250 RPM, together with 66.7 grams of Mogul L carbon black (Cabot), 6.7 grams of BT583D (blue pigment produced by Cookson), 5 grams of aluminum tri stearate and an additional 1459.6 grams of Isopar L, for eight hours at 30°C.

3) Continuation of Grinding

34.5 grams of ACumist A-12 is added and grinding is continued for an additional 4-12 hours. The resulting particles are fibrous particles having a measured diameter in the range of 1-3 micrometers.

The resulting material is diluted with additional Isopar L and Marcol 82 to give a working developer in which the dry solids portion is about 1.7% and in which the overall ratio of Isopar L to Marcol is between about 50:1 and 500:1, normally about 100:1.

Charge director as described in US patent application 07/915,291 (utilizing Lecithin BBP and ICIG3300B) and in WO 94/02887, in an amount equal to 40 mg/gm of solids, is added to charge the tone particles. Other charge directors and additional additives, as known in the art may also be used.

In a preferred embodiment of the invention the substrate is printed using an intermediate transfer member to transfer images to the substrate and to fuse and fix them

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thereto. Preferred apparatus for such printing are the E-Print 1000 and the E-Print Omnius printers marketed by Indigo NV.

5 The present invention has been described utilizing preferred embodiments thereof. It should be understood that the details of the coating processes and exact formulations of the coatings and liquid toners are meant to be exemplary in nature and not to limit the claims. In particular the invention also includes materials which are listed in the summary and claims for the substrate, the underlayer, the overlayer and the toner, as well as different combinations of materials chosen from the four groups of materials.

PDN

CLAIMS

1. A substrate suitable for printing a toner image thereon, comprising:
a sheet of plastic;
an underlayer coating, on the sheet of plastic, comprising a first polymer material;
5 an overlayer coating, on the underlayer, comprising a second polymer material and
having an outer surface to which a toner image can be fused and fixed.
2. A substrate according to claim 1 wherein the sheet of plastic is PET.
- 10 3. A substrate according to claim 1 wherein the sheet of plastic is BOPP.
4. A substrate according to claim 1 wherein the sheet of plastic is polyethylene.
5. A substrate according to claim 1 wherein the sheet of plastic is vinyl.
- 15 6. A substrate according to claim 1 wherein the sheet of plastic is polycarbonate.
7. A substrate according to any of the preceding claims wherein the overlayer comprises
ethylene acrylic acid copolymer.
- 20 8. A substrate according to claim 7 wherein the ethylene acrylic acid copolymer has an
acrylic acid comonomer percentage weight of less than 18%.
9. A substrate according to claim 7 wherein the ethylene acrylic acid copolymer has an
25 acrylic acid comonomer percentage weight of less than 16%.
10. A substrate according to any of claims 7-9 wherein the ethylene acrylic acid copolymer
~~has an acrylic acid comonomer percentage weight of more than 8%.~~
- 30 11. A substrate according to any of claims 7-9 wherein the ethylene acrylic acid copolymer
has an acrylic acid comonomer percentage weight of more than 12%.

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12. A substrate according to any of claims 1-6 wherein the overlayer comprises polyvinyl pyridine.
13. A substrate according to any of claims 1-6 wherein the overlayer comprises styrene butadiene copolymer.
14. A substrate according to any of the preceding claims wherein the underlayer comprises amine terminated polyamide.
15. A substrate according to any of claims 1-13 wherein the underlayer comprises a silane coupling agent.
16. A substrate according to any of claims 1-13 wherein the underlayer comprises amino propyl triethoxy silane.
17. A substrate according to any of the preceding claims wherein the underlayer has a weight of between 0.1 and 1 grams per square meter.
18. A substrate according to any of the preceding claims wherein the underlayer has a weight of between about 0.3 and 0.5 grams per square meter.
19. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.1 and 10 grams per square meter.
20. A substrate according to any of the preceding claims wherein the overlayer has a weight of between 0.2 and 2 grams per square meter.
21. A substrate according to claim 20 wherein the overlayer has a weight of between about 0.25 and about 0.35 grams per square meter.
22. A method of producing a coated substrate which a toner image can be adhered comprising:

coating a sheet of plastic with a first polymer material as an underlayer;

overcoating the underlayer with an second polymer material to form an overlayer coating on the underlayer, the overlayer having an outer surface to which a toner image can be adhered and fixed.

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23. A method according to claim 22 wherein the coated substrate is a substrate according to any of claims 1-21.

24. A substrate produced according to the method of claim 22.

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25. A substrate comprising a sheet chosen from the group consisting of PET, BOPP, polycarbonate, polyethylene and vinyl and an outer coating chosen from the group consisting of ethylene acrylic acid copolymer, polyvinyl pyridine and styrene butadiene copolymer.

15 26. A substrate according to claim 25 wherein the sheet is a PET sheet.

27. A substrate according to claim 25 wherein the sheet is a BOPP sheet.

28. A substrate according to claim 25 wherein the sheet is a polycarbonate sheet.

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29. A substrate according to claim 25 wherein the sheet is a polyethylene sheet.

30. A substrate according to claim 25, wherein the sheet is a vinyl sheet.

25 31. A substrate according to any of claims 25-30 wherein the coating comprises polyvinyl pyridine.

32. A substrate according to any of claims 25-30 wherein the coating comprises styrene butadiene copolymer.

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33. A substrate according to any of claims 25-30 wherein the coating comprises ethylene acrylic acid copolymer.

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34. A substrate according to claim 33 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 18%.

5 35. A substrate comprising a sheet and a coating of ethylene acrylic acid copolymer having an acrylic acid comonomer percentage weight of less than 18%.

36. A substrate according to any of claims 33-35 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of less than 16%.

10 37. A substrate according to any of claims 33-36 wherein the ethylene acrylic acid copolymer has an acrylic acid comonomer percentage weight of more than 8%.

38. A substrate according to any of claims 33-37 wherein the ethylene acrylic acid
15 copolymer has an acrylic acid comonomer percentage weight of more than 12%.

39. A substrate according to any of claims 25-38 wherein the coating has a weight of between 0.1 and 0.4 grams per square meter.

20 40. A substrate according to claim 39 wherein the coating has a weight of between about 0.25 and about 0.35 grams per square meter.

41. A printing method comprising:
providing a substrate according to any of claims 1-21 or 24-40; and
25 printing a toner image on the substrate.

42. A printing method according to claim 41 wherein the toner image is a liquid toner
image.

30 43. A printing method according to claim 41 or claim 42 wherein printing comprises transferring the toner image to the substrate using heat and pressure.

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44. A printing method according to claim 41 or 42 wherein printing comprises electrostatically transferring the toner image to the substrate.

45. A printing method according to any of claims 41-44 and comprising:

- 5 forming the image on an image forming surface;
transferring the image from the image forming surface to an intermediate transfer member; and
transferring the image from the intermediate transfer member to the substrate.

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ABSTRACT

A substrate suitable for printing a toner image thereon, comprising:

a sheet of plastic;

an underlayer coating, on the sheet of plastic, comprising a first polymer material; and

5 an overlayer coating, on the underlayer, comprising a second polymer material and having an outer surface to which a toner image can be adhered and fixed.

